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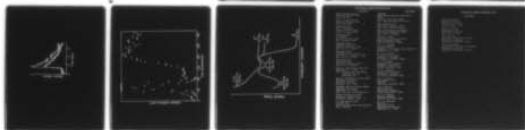
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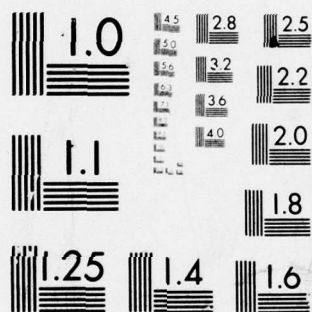
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Unimolecular Decay of Photoexcited
Tetramethyldioxetane Probed by Picosecond Spectroscopy

by

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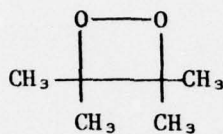
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Abstract

The photolysis of tetramethyldioxetane at 264 nm was probed using picosecond spectroscopic techniques. Singlet excited acetone was one of the observed products. The rise time for acetone fluorescence was determined to be less than 10 psec. A mechanism consistent with these results is proposed.

Introduction

Nearly all photochemical reactions proceed to form products directly in the ground electronic state. One of the noted exceptions to this generalization is tetramethyl-1,2-dioxetane (**1**). It has been reported that photolysis of **1** leads to direct formation of electronically excited acetone of both singlet and triplet multiplicity.¹ In this paper we report the results of our investigation of this unusual photochemical reaction by picosecond spectroscopy.



1

Experimental

A train of 10 picosecond pulses at 1056 nm was generated with a neodymium phosphate laser (Holobeam). A single pulse was extracted and amplified and the second harmonic was produced with a type II KDP crystal (Lasermetrics). The residual infrared light was removed with suitable filters. The green light passed through an angle tuned ADP crystal (Lasermetrics) to produce radiation at 264 nm. The major portion of the green light was eliminated by reflection of the ultraviolet pulse with a dichroic beamsplitter. A quartz plate reflected ~8% of exciting light into a vacuum photodiode which was used to trigger a streak camera (Hamamatsu). The residual green light was removed from the excitation path by means of a Glan-air prism, a Corning 7-54 color filter and a second dichroic mirror. The excitation was focused to a small spot in the 2 mm pathlength sample cell. The fluorescence emission was detected at the rear of the cell with one to one imaging optics. The optics imaged the emitted light on the 30 micron slit of the streak camera. The

output of the streak camera was coupled to a SIT vidicon camera. For long time scale experiments a microprocessor controlled digitizer (RKB) was used. Due to the weak fluorescence intensity, the signal recorded at the fastest streak speeds was of a magnitude comparable to the noise. Consequently, computer averaging was required to enhance the signal to noise ratio. For this purpose a vidicon digitizer constructed in our electronics shop, was interfaced to a Nova 3 computer. Because of the very low signal to noise ratio we could not accurately determine the onset of the fluorescence. Therefore, a small part of the green light that passed through the first dichroic mirror was reflected on a path parallel to the excitation beam. The optical pathlength of the green light was adjusted so that it arrived about 70 psec before the ultraviolet excitation pulse. In this fashion an accurate reference independent of the streak camera jitter could be obtained. The fast streak speeds of the temporal disperser were calibrated with an echelon. The apparatus is shown schematically in Figure 1.

The dioxetane was synthesized by the procedure of Kopecky² and purified by sublimation and recrystallization from pentane. The solvent used was acetonitrile (Spectrograde, Aldrich) which showed negligible impurity fluorescence. There was no detectable change in the absorption spectrum of the dioxetane sample following the picosecond experiments. This indicated that insignificant thermal or photochemical decomposition had occurred. Steady state fluorimetry was performed on a Farrand Mark I Spectrofluorometer.

Results

The fluorescence emission spectrum of acetone and dioxetane λ in air saturated acetonitrile solution are superimposable with a maximum at ca. 400 nm. Chemical trapping experiments³ have confirmed that singlet

excited acetone results from photolysis of λ . The time dependence of the fluorescence for λ and for acetone is shown in Figure 2. The emission lifetime for both samples was the same within experimental error and equal to ca. 2 nsec*, consistent with the reported lifetime of acetone singlet.⁴

The initial rise of the fluorescence intensity for dioxetane λ is shown in Figure 3. Within the resolution of the apparatus the fluorescence appeared coincident with the 264 nm pulse. The intense spike in this figure is due to the green reference pulse which permits us to establish a time base from shot to shot and also to monitor the quality of the laser pulse. This pulse has a fullwidth at half height of about 20 psec. This does not represent the true temporal profile of the laser but is broadened by the temporal disperser and distortion of the image in the SIT vidicon camera. Using the observed reference pulse the fluorescence from dioxetane λ could be deconvoluted from the exciting pulse. This procedure showed that the rise time for acetone fluorescence from this molecule is less than ca. 10 picoseconds.⁵

The possibility that the observed results are due to fluorescence of both the dioxetane and single acetone was examined. The observed fluorescence decay is identical to that of acetone (Figure 2). Since dioxetane absorbs much further in the red than acetone, it is unlikely that emission from singlet dioxetane escaped observation. The reasonable conclusion from these observations is that the rise in fluorescence emission is due to the formation of an excited acetone fragment.

* Due to the low intensity of the fluorescence, it was not possible to spectrally resolve the emission decay.

Discussion

In considering the plausible mechanistic details for the unusual photochemical generation of singlet excited acetone from dioxetane 1_{λ} , several experimental observations are of importance. First, our temporal resolution of the fluorescence indicates that there can be no intermediate species with a lifetime greater than ca. 10 psec between the state formed by absorption and the emitting acetone singlet. Second, our comparison of the fluorescence intensity generated by irradiation of 1_{λ} and of acetone qualitatively confirms the observation that the yield of singlet acetone from 1_{λ} excited at 264 nm is no more than ca. 30% (see figure 3). Third, the yield of acetone singlet from photoexcited 1_{λ} is wavelength dependent, being higher at shorter wavelengths.¹

Recent studies of the chemiluminescence of 1,2-dioxetanes have indicated that the 1,4-biradical formed by cleavage of the oxygen to oxygen bond precedes chemical formation of excited states, at least for the triplet products.⁶ Unless this intermediate has a lifetime of 10 psec or less, the thermal and photochemical reactions to form excited acetone must proceed by different paths. This conclusion is confirmed by the observation that the ratio of triplet to singlet acetone from the photolysis is much lower than the corresponding ratio from the thermolysis.⁷ In addition, it is difficult to rationalize the wavelength dependence of the singlet yield if a common biradical intermediate were present.

Figure 4 is a two dimensional representation of the multidimensional reaction surfaces for the thermal and photochemical reactions of dioxetane 1_{λ} . This figure is consistent with the three key observations concerning dioxetane photochemistry. Absorption of an energetic photon supplies

sufficient energy to dissociate $\frac{1}{\nu}$ to excited acetone instantaneously if the excess energy is concentrated in the reactive vibrational modes. Competitive with dissociation, vibrational relaxation through non-reactive modes funnels the excited state of dioxetane to a position on the surface from which it internally converts to the biradical intermediate with which the excited dioxetane correlates.⁸ The biradical formed by this process may then go on to excited acetone just as in normal chemiluminescence. This route leads to triplet acetone as the predominant product.

The wavelength dependence of dioxetane photochemistry is explained by this model as a competition between direct dissociation and vibrational relaxation which leads to the biradical. With more energetic photons the dissociative process is favored leading to the observed increased yield of acetone excited singlet state. The energy difference between the singlet and triplet biradicals is expected to be small. Thus, the rate of inter-system crossing of this intermediate should be rapid. Coupled with the unit quantum efficiency for photochemical decomposition, this model suggests that the barrier for reformation of dioxetane is higher than the decomposition of the biradical to excited acetone. If the barrier to reclosure was not the greater, a portion of the biradical could return to the ground state dioxetane resulting in a quantum yield for dioxetane disappearance of less than one.

Our interpretation of the photochemistry of dioxetane $\frac{1}{\nu}$ implies that singlet and triplet excited acetone are formed by different but parallel routes. Experiments designed to probe the rise time of directly formed acetone triplet from the irradiation of $\frac{1}{\nu}$ are underway.

Acknowledgment

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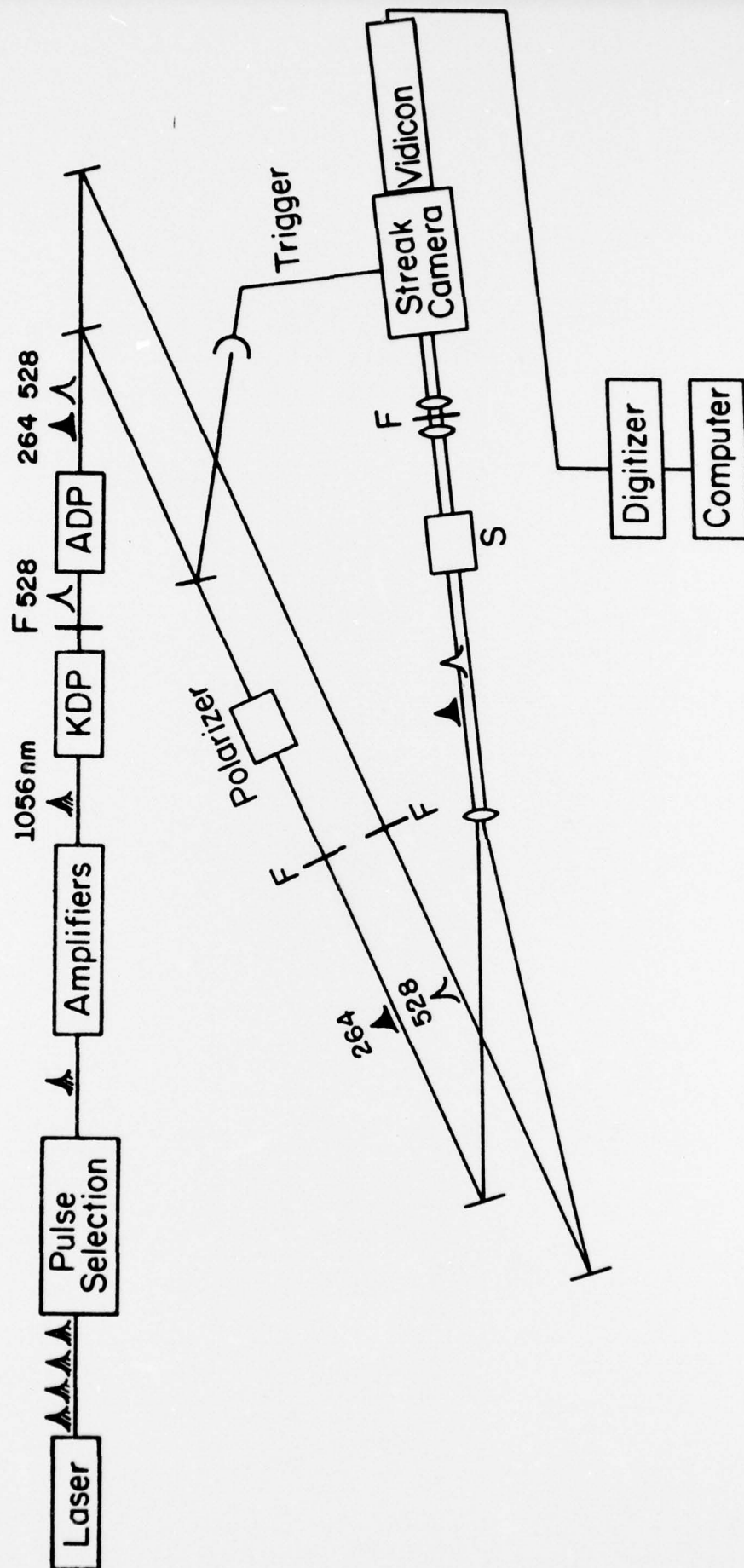
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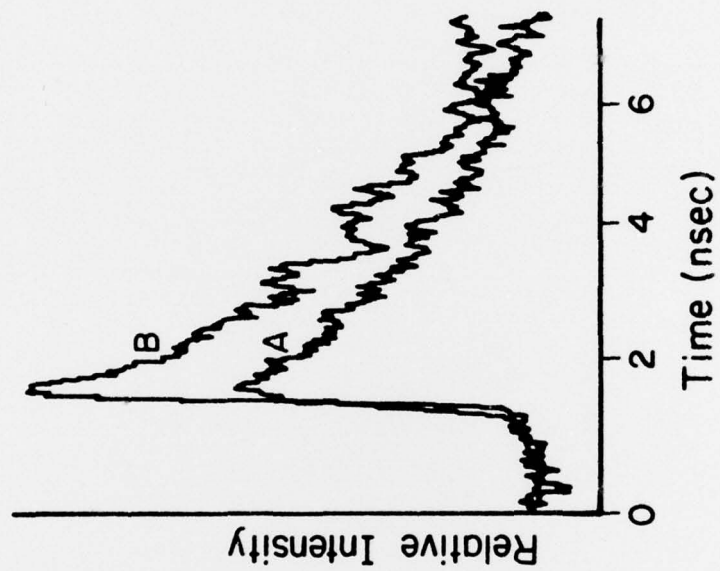
Figure 1. Block diagram of Laser apparatus; S = Sample, F = Filters.

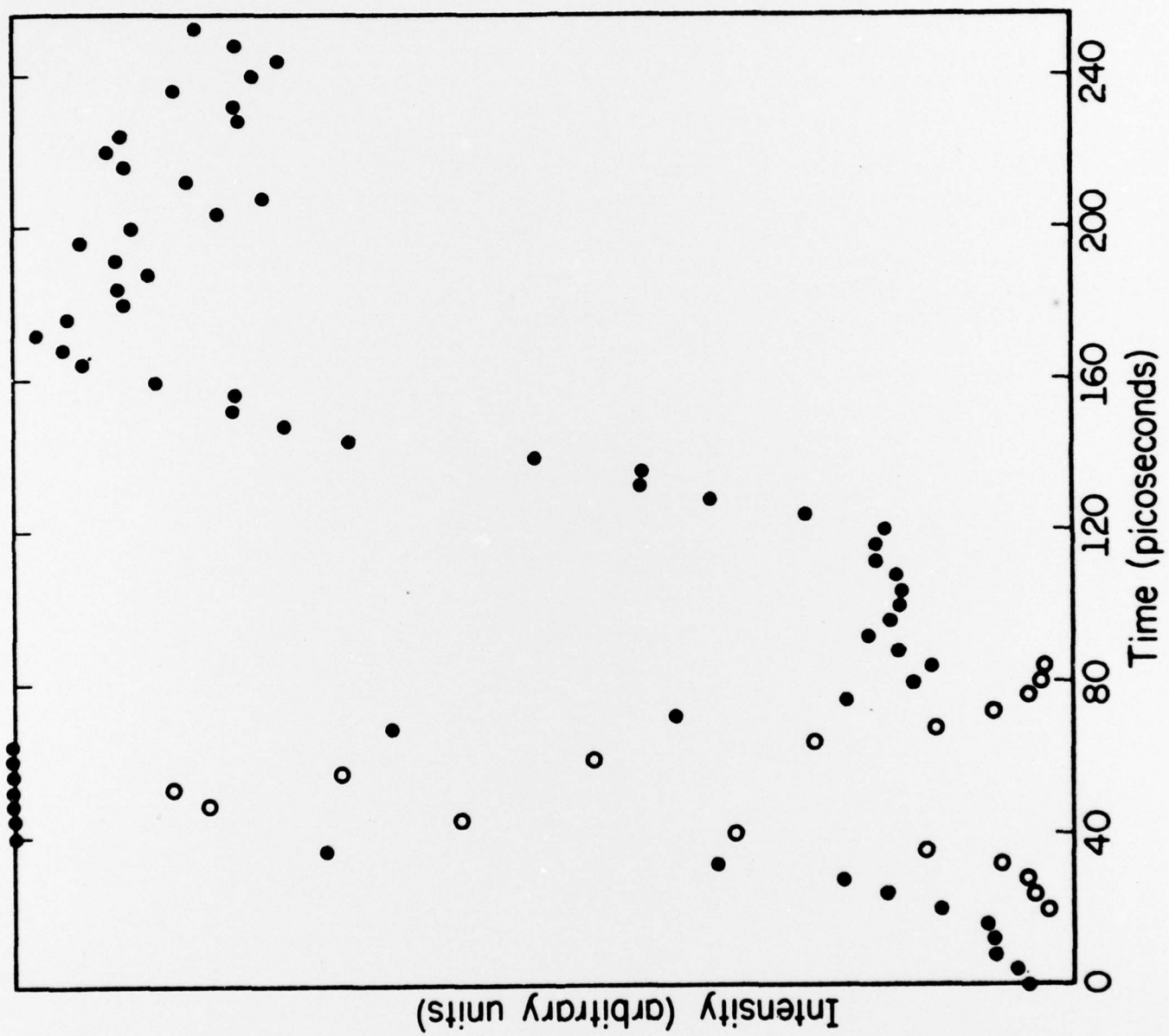
Figure 2. Fluorescence decay from photoexcited acetone (A) and photoexcited dioxetane (B).

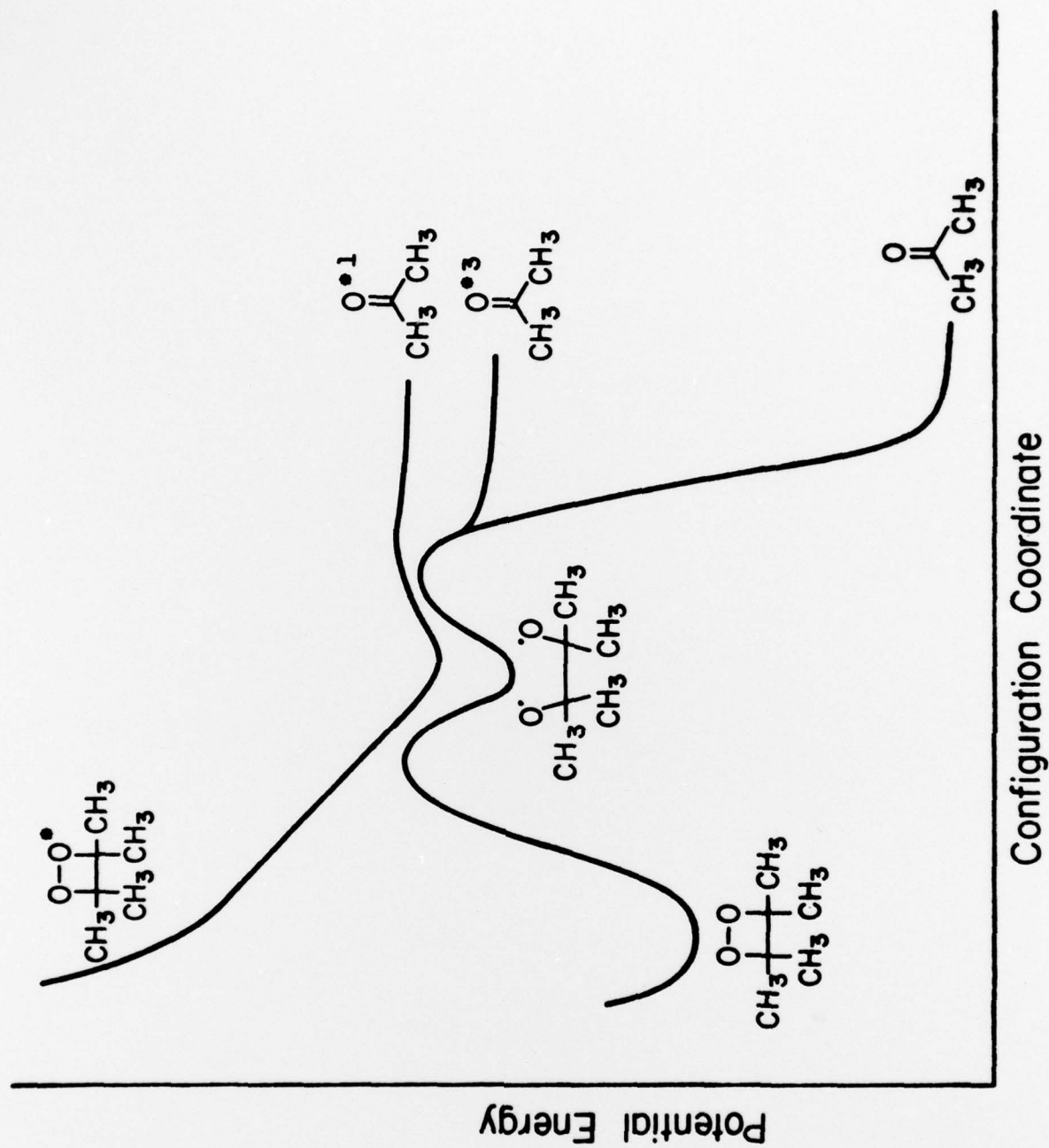
Figure 3. Rise time of acetone fluorescence from excitation of dioxetane. Note that the intense spike on the left is the green reference pulse.

Figure 4. Schematic reaction coordinate diagram for the thermal and photochemical reactions of dioxetane 1.
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